INTERCOMPARISON OF SURFACE MEASUREMENT AND SATELLITE OBSERVATION OF OZONE AND ITS PRECURSORS (CO, NO_x, VOCs) AND ESTIMATION OF THEIR IMPACT ON CROP YIELD

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SONAL KUMARI

Prof. K. MAHARAJ KUMARI

Supervisor

Prof. SAHAB DASS

Head, Department of Chemistry

Prof. RAVINDER KUMAR

Dean, Faculty of Science

FACULTY OF SCIENCE
DAYALBAGH EDUCATIONAL INSTITUTE
(DEEMED UNIVERSITY)
DAYALBAGH, AGRA-282005

INTRODUCTION

Industrialization, urbanization, rapid traffic growth and increasing levels of anthropogenic emissions in the last two decades have resulted in a substantial deterioration of air quality. The changing composition of the atmosphere is of particular interest since some of the minor constituents (trace gases) of air can affect the earth's energy balance (Dentener et al., 2005). The greenhouse gases absorb infrared radiation and can therefore trap the outgoing long wave radiation leading to changes in the climate system (e.g. increasing the temperature near the surface, changing the hydrological cycle through increased evaporation etc.). Several greenhouse gases have increased significantly which cause the (direct) anthropogenic greenhouse effect (Harries et al., 2001). In addition to carbon dioxide (CO_2), methane (CH_4) and ozone (O_3) are also important contributors to greenhouse effect (IPCC 2007). Additionally, ozone is a toxic gas which can have detrimental effects on human health and crops (Solomon, 2008). Stratospheric input and photochemical ozone formation in the troposphere are the two main sources determining the ozone levels in the surface layer of the atmosphere (Sicard et al., 2009). The relation between ozone and its main precursors represent one of the major scientific challenges associated with urban air pollution. Therefore, understanding the processes that control origin, trends and distribution of tropospheric ozone has become important in atmospheric chemistry. Over the past decade, observation of tropospheric ozone and its precursors from space has become an increasingly powerful tool for understanding the ozone budget (Martin, 2008). Now a days, satellite based observations are available for monitoring atmospheric trace gases all over the globe. Current satellite instruments provide reliable measurements of ozone, CO and NO_2 (Fishman et al., 2008).

About 90% of the atmospheric ozone is present in the stratosphere and only about 10% resides in the troposphere. Despite this relatively small fraction, ozone governs the chemistry of the atmosphere. Ozone plays a key role in biogeochemical cycles, air quality, and global change. Ozone in the lower troposphere is mainly produced by photochemistry involving pollutants that are released from various industrial and other

anthropogenic activities (Ryerson et al., 2001). Photochemical production is non-linearly dependent on the levels of precursors (Lin et al., 1988). Depending upon the precursorôs strength and photochemical reactions, tropospheric ozone varies spatially and temporally over the globe (Nishant et al., 2014). Tropospheric ozone (O_3) is regulated by the US Environmental Protection Agency (US EPA) as a criteria pollutant (EPA, 2006). O_3 is unique among criteria pollutants because it is formed in the atmosphere rather than directly emitted. Ozone is produced in the troposphere by gas-phase oxidation of hydrocarbons and CO catalyzed by hydrogen oxide radicals (HO_x=OH+H+peroxy radicals) and nitrogen oxide radicals (NO_x=NO+NO_2). In polluted regions with large sources of NO_x and hydrocarbons, high concentrations of O_3 in surface air represent a major air pollution problem (Monks et al., 2015). As a pollutant and greenhouse gas, O_3 should be brought under effective control, but the variability of its natural background level in the boundary layer makes difficult the definition of the concentration above which it becomes a pollutant (Ahammed et al., 2006). Rise in concentration of ozone negatively affects growth of crop and is most likely to threaten food production in future (Sinha et al., 2015). Tropospheric ozone concentrations and growth rates exhibit large spatial and temporal variabilities. Tropospheric O_3 is also of global interest as the primary source of OH (the main atmospheric oxidant). Solar UV radiations of wavelength ’ 320 nm dissociate the ozone molecules into O^1D which react with water vapours in atmosphere to produce OH radicals that are oxidizing in nature. These radicals react with non methane hydrocarbons (NMHCs), CO, NO_x, CH_4 controlling their concentrations in atmosphere (Atkinson, 2000). NO_x, volatile organic compounds (VOCs) and OH are the precursors for formation of O_3 and photo-oxidants (Jonson et al., 2006).

The increase of industrial activity, vehicular traffic and agricultural activities over the last century has resulted in a strong increase of emissions of carbon monoxide, nitrogen oxides, methane and volatile organic compounds (VOCs). These pollutants get oxidized in series of complex sunlight initiated reactions to produce secondary pollutants including ozone, peroxyacyl nitrates, carboxylic acids, carbonyls and secondary aerosols (Reddy et al., 2010). Among them ozone is the most studied secondary pollutant, for which many countries has issued a national ambient air quality standard (NAAQS). Since ozone

production in the atmosphere is mainly by oxidation of its precursors, control strategies for ozone air quality must involve control of the emissions of primary pollutants, namely VOCs and NO_x. Initial step in assessing ozone level in the atmosphere is identification of VOCs and measuring the concentrations of VOCs, CO and NO_x (Atkinson, 2000).

Ozone levels at a given site are influenced by several factors: (i) background concentrations of ozone and precursor gases, which are determined by large-scale processes, such as stratosphere-troposphere exchange (Ganguly and Tzanis, 2011), and global to hemispheric-scale precursor emissions (ii) regional and local emissions. High concentrations of tropospheric ozone was initially thought to be restricted to urban areas only, but studies at rural areas also show increased levels of tropospheric ozone (Wang et al., 2001).

Tropospheric O_3 is produced by photolysis of NO_2 (in presence of sunlight) and get destructed by titration with NO, resulting in no net O_3 production (Lal et al., 2000) but a reaction that converts NO in NO_2 without consuming an O_3 molecule could make ozone accumulate. This reaction occurs in the presence of hydrocarbons. In particular, peroxy radicals ($RO_2^{Å}$, where R is an alkyl group) produced during the oxidation of hydrocarbon molecules react with NO to form NO_2, allowing a greater production of ozone (Swamy et al., 2012).

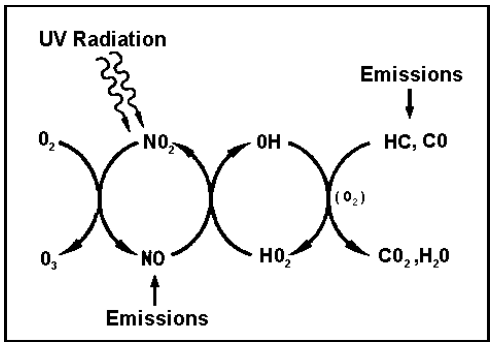

Figure 1.Tropospheric ozone chemistry

To obtain a better understanding of the global tropospheric ozone levels, it is important that a clear picture of its global distribution is to be obtained. For this several observational techniques have been developed using information from satellite measurements. In recent years tropospheric column ozone study has been done using

satellite observations measured by the TOMS (Total Ozone Mapping Spectrometer) instrument, MOPITT(Measurement of Pollution in the Troposphere), Aura satellite showing a great agreement in the observed and satellite data (Fishman et al., 2003, Ghude et al., 2011). All satellite observations of tropospheric ozone and its precursors so far have been from sun synchronous low earth orbit (LEO). Aura is designed to make comprehensive stratospheric and tropospheric composition measurements from its four instruments, the High Resolution Dynamics Limb Sounder (HIRDLS), the Microwave Limb Sounder (MLS), the Ozone Monitoring Instrument (OMI), and the Tropospheric Emission Spectrometer (TES) (Schoeberl et al., 2006). The Aura satellite includes direct measurements of tropospheric ozone by two instruments measuring in different spectral regions: the Tropospheric Emission Spectrometer (TES) in the thermal infrared (TIR) (Beer, 2006) and the Ozone Monitoring Instrument (OMI) in the UV (Levelt et al., 2006, Liu et al., 2010). TES is a Fourier transform IR spectrometer with high spectral resolution (0.1 cm^{-1} apodized in nadir) and a wide spectral range (650– 3050 cm^{-1}). The TES investigation is especially focused on mapping the global distribution of tropospheric ozone and on understanding the factors that control ozone concentrations. OMI is an ultraviolet/visible (UV/VIS) nadir solar backscatter spectrometer, which provides nearly global coverage in one day with a spatial resolution of 13 km x 24 km.

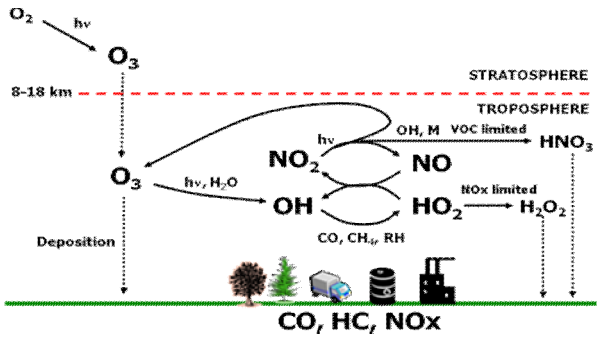

Figure 2. Schematic of tropospheric O_3 chemistry illustrating the coupling between the chemical cycles of ozone, HO_x and NO_x (Jacob 2000).

OZONE PRECURSORS

1. Volatile Organic Compounds (VOCs)

Volatile organic compounds include a large variety of carbon-based molecules such as aldehydes, ketones and light hydrocarbons. They can be classified into three groups in terms of volatility: (*i*) very volatile organic compounds with a boiling point (BP) ranging from 0°C to 100°C, (*ii*) volatile organic compounds with a BP value of 100ï 240°C and (*iii*) semi-volatile organic compounds with a BP value of 240ï 400°C. Volatile organic compounds (VOCs) of biogenic or anthropogenic origin are known to play an essential role in the photochemistry of the polluted boundary layer (IPCC 2007). Sharing the same characteristics of high volatility in the ambient environment VOCs result in alteration of the chemistry of atmosphere. The main anthropogenic sources of VOCs include industries, vehicles and building materials, while vegetation, microorganisms and other biological activities are identified as their natural sources (Cai et al., 2010). The main concern of VOCs is the role they play in the formation of ozone and photochemical smog and increased risk of cancer. Depending on VOC/NO_x ratios, O_3 can be produced or consumed. When VOC/NO_x ratio is high (NO_x sensitive) O_3 increases with increasing NO_x and changes little with increasing VOCs. On the other hand when VOC/NO_x ratio is low (VOC sensitive) O_3 increases with increasing VOCs and decreases with increasing NO_x (Sillman, 1999). Temperature increase enhances biogenic emissions of isoprene and other VOCs as well as photochemical activity since most thermal atmospheric reactions show positive temperature dependence. Thus, temperature increase in the presence of sufficient NO_x leads to the increase in O_3 level (Im et al., 2011). Certain VOCs such as alkenes are more reactive than alkanes and, in the hours immediately after emission, they can contribute more to ozone formation per unit mass. As a result, VOC have been ranked according to their ozone formation potential and incremental contributions to ozone production (Carter, 1994). VOCs emitted to the atmosphere are oxidized photochemically by a succession of steps leading eventually to CO_2 and H_2O. Formaldehyde is a high-yield intermediate of this oxidation chain.

Carbonyls

Carbonyls, including aldehydes and ketones, are the important classes of oxygenated volatile organic compounds (OVOCs) in the global atmosphere. Carbonyls are among the major species of organic compounds involved in photochemical air pollution since aldehydes and ketones play an important role as products of photo-oxidation of gas-phase hydrocarbons, as a major source of free radicals (Grosjean, 1998). The photo-dissociation of carbonyls, in particular formaldehyde, is an important source of free radicals (Atkinson and Arey, 2003). In addition, the degradation of carbonyls can produce ozone (O_3) and peroxyacyl nitrates (PANs) (Roberts et al., 2001). Carbonyls can be produced both by oxidation of other VOC species and by direct emission into the atmosphere from a variety of anthropogenic and natural sources, such as biogenic emission (Hellén et al., 2004), vehicular exhaust (Ho et al., 2012), biomass burning (Hall et al., 2012) and industrial emissions (Zheng et al., 2013). Emission of carbonyls from vehicular exhaust is substantial relative to emissions of alkenes from vehicular exhaust. However, the production of aldehydes from alkanes is relatively small compared to their production from alkenes (Altshuller, 1993). Aldehyde sources in the atmosphere include primary emissions from natural vegetation, industrial plants, incinerators and vehicles, as well as secondary ones via photo-oxidation of methane, isoprene and other biogenic and anthropogenic hydrocarbons (IPCS 2002).

Aldehydes, mainly formaldehyde and acetaldehyde, the two most abundant aldehydes in ambient air are ubiquitous in urban atmospheres, where they are introduced through a variety of different pathways (Bakeas et al., 2003). Formaldehyde (HCHO) is an important intermediate in the photochemical oxidation of atmospheric hydrocarbons. In unpolluted rural areas the dominant source of formaldehyde in the free troposphere is the reaction of methane. Photolysis is on the other hand an important sink for HCHO, which, depending on the wavelength, yields H atoms and HCO radicals or hydrogen and carbon monoxide (Riedel et al., 1999).

$HCHO + hv\ (325\ nm) \longrightarrow H + HCO$

$HCHO + hv\ (325\ nm \leq \lambda \leq 360\ nm) \longrightarrow H_2 + CO$

Formaldehyde is also linked with the so-called odd hydrogen family (OH, HO, H) by the following reactions:

$HCO + O_2 \longrightarrow HO_2 + CO$

$CO + OH + M \longrightarrow H + CO_2 + M$

$H + O_2 + M \longrightarrow HO_2 + M$

With regard to these reactions, formaldehyde has to be considered as a significant radical source.

Carbonyls are of great significance to atmospheric chemistry due to the strong influence these species have on photochemical reactions that lead to the formation of important smog components such as nitric acid, peroxyacetylnitrate (PAN), and many others. In the last three decades, the aldehydes, especially formaldehyde, have received a great deal of attention due to their recognized mutagenic and carcinogenic nature and their toxic activity associated with eyes and respiratory tract irritations, nausea, headache, tiredness and thirst (WHO, 2010).

2. Nitrogen oxides (NO_x)

Nitrogen oxides (NO and NO_2) play an important role in ground-level O_3 concentrations (Schultz et al., 1999). Greater NO_2 concentrations give rise to O_3 levels due to its photolysis, while NO serves as the major source for the production of NO_2 as it is oxidized in the presence of sunlight and VOCs (Lin et al., 2005). The oxides of nitrogen, NO_x (NO + NO_2) are mainly emitted in the atmosphere as NO, which is subsequently transformed into NO_2 and other nitrogenous species. Nitrogen oxides play a central role in photochemical production of ozone in the troposphere. The dominant source of NO_x in the atmosphere is fossil fuel combustion, biomass burning, emission from soil and by

lightning activity (Schumann and Huntrieser, 2007). Levels of O_3 are expected to increase at low NO_x, reaching a maximum and then decrease at high NO_x concentration (Sillman et al., 1990). This behavior is understood in terms of the dual role of NO_x in photochemical O_3 production: NO_x is a catalyst yielding O_3 from photolysis of NO_2 produced from reactions of peroxy radicals with NO. However, at high NO_x concentration, the reaction

$OH + NO_2 \longrightarrow HNO_3$ inhibits O_3 production (Kleinman et al., 2002). However, NO can also be an important O_3 sink through its reaction with ozone, known as ozone titration, especially during nighttime.

3. Carbon Monoxide (CO)

Carbon monoxide (CO) is an important trace gas in the troposphere as it plays a crucial role in atmospheric photochemistry through its reaction with highly reactive hydroxyl radicals (OH). It is the most important sink of OH radicals in the unpolluted atmosphere (Savage et al., 2001). The OH radicals act as a detergent for several pollutants and greenhouse gases (methane and other hydrocarbons). An enhancement in CO will decrease OH radicals and increase the lifetime of these trace constituents. In addition, CO is one of the main precursors of secondary pollutant ozone (O_3) in NO_x rich environment and affects the ambient air quality (Crutzen and Zimmermann, 1991). Though CO is not a direct greenhouse gas, it does have a global warming potential because of its effects on the lifetime of several greenhouse gases (Daniel and Solomon, 1998). The main sources of CO are both natural and anthropogenic, including combustion processes near the surface (transport, power plants, domestic heating and biomass burning) and oxidation of methane and other non-methane hydrocarbons (Duncan et al., 2007). The presence of CO facilitates the production of NO_2 through the oxidation by OH, thus results in greater O_3 concentration (Lin et al., 2005). CO is a useful tracer of transport due to its long photochemical lifetime of 2-3 months (Xiao et al., 2007). The satellite based measurements are found to be useful in the study of vertical distribution and long range transport of CO on a global scale (Edwards et al., 2006).

LITERATURE REVIEW

The gaseous environment surrounding the earth mainly comprises of N_2, O_2, Ar and some minor and trace gases as constituents. These gases support life, protect human from harmful solar UV-radiations, regulate thermal budget and chemistry of atmosphere. Among trace gases ozone is the most important gas (Lal et al., 2007). Population growth and increasing industrialization in the last two decades has inevitably resulted in higher demand for energy, greater use of fossil fuels and more emission of pollutants into the atmosphere. Large increment in total energy consumption in Asia in the last two decades has resulted in rapid growth in emission of pollutants (BC, CO, VOCs, SO_2, NO_x) in atmosphere. Ohara et al., 2007 reported that total emission of SO_2, NO_2 and NMHCs in Asia has increased by 22%, 44% and 99% respectively over 2000 levels. CO, VOCs and NO_x emitted in the troposphere results in increment of tropospheric O_3, which has important impact on peopleôs health (Shao et al., 2009; Chang et al., 2014). A number of studies reporting ambient O_3 and its precursors level has been done throughout the globe (Bonasoni et al., 2000; Ran et al., 2009; Iqbal et al., 2014; Lal et al., 2013; Jena et al., 2015). Studies reporting hourly measured surface ozone levels exceeding the World Health Organization (WHO) ambient air quality standards (hourly average of 80 ppb) are observed which shows serious ozone pollution (Jain et al., 2005; Al-Jeelani, 2014). To properly understand the role of these compounds in urban photo-oxidation and the associated health hazards associated, detailed knowledge of their presence in ambient air is required (Kumar and Viden, 2007).

Seasonal and diurnal variation of O_3, its precursors and meteorological parameters has been extensively studied around the world (Saito et al., 2002; Lehman et al., 2004; Abdul Wahab et al., 2005; Tu et al., 2007; Mahapatra et al., 2012). These studies have improved the knowledge of the processes and factors affecting the ozone formation and losses. The temporal variation of O_3 has been reported at many sites including rural, urban, coastal and mountains (Lal et. al., 2000; Nair et. al., 2002; Debaje et. al., 2003; Naja et. al., 2003; Satsangi et. al., 2004; Fujita et al., 2012; Chen et al., 2013; Cristofanelli et al., 2015). The

unique meteorology of mountain site plays an important role in O_3 chemistry. Lower mixing ratios were observed during day time at mountain top (Guru Shikhar) at Mt. Abu (Naja et al., 2003). In contrast at an urban site (Beijing, China) a significant peak is found during noon with seasonal maxima in winters (Chen et al., 2013) while at rural site Anantapur (India) highest O_3 concentrations are observed in summers (Ahammed et al., 2006).

In diurnal cycle O_3 concentration starts increasing after the sunrise, reaching a peak value at noon time and thereafter drops by the evening (Swamy et al., 2012). The photochemical oxidation of precursors in presence of sufficient amount of NO_x and increased boundary layer height at noon results in increased mid day concentrations of O_3. The thermal stratification and convective heat transfer to the surface from air at higher altitudes results in increasing O_3 mixing ratio with rising boundary layer. O_3 show positive correlation with temperature and solar radiation therefore noon time O_3 concentration is higher when temperature and solar radiation shows peak value (Beig et al., 2008). During late evening and night, chemical loss of O_3 by NO titration and suppressed boundary layer results in low O_3 concentration. At night lower value of O_3 is observed as there is no possibility of O_3 formation by photochemical oxidation (Beig et al., 2007). High levels of ozone during night time in winter at Mt. Cimone (Italy) was observed by Bonasoni et al., 2000 which was mainly due to strong temperature inversion observed after sunset, that triggers the formation of wind maximum above the inversion layer. This meteorological phenomenon is called low-level jet. Mechanical turbulence produced by the jet mixes up ozone rich air from aloft to the ground.

Variations in amplitude of daytime O_3 concentration are observed during different seasons (Beig et al., 2007). At a semi-urban site (Pune) a prominent and sharper increment in noon time O_3 concentration was observed during winters while in summers a broader peak was observed. The higher and sharper noon time peak in winter was due to higher NO_x mixing ratios resulting into higher O_3 production and also facilitating faster NO titration during evening and night.

A comparative study at urban, sub-urban and rural site of Shanghai, China was reported by Geng et al., 2008 during 2006-2007. Highest average O_3 concentration was observed at sub-urban site (35 ppbv) followed by rural site (32 ppbv) and minimum at urban site (12 ppbv). The sub-urban site showed maximum concentration because of a chemical industry located in the vicinity which was a significant VOCs emission source. The unusual trend observed at rural and urban site was because of O_3 depression processes observed at urban site.

Precursors NO_x, VOCs and CO show diurnal pattern opposite to O_3 (Lal et al., 2000; Kleinman et al., 2002; Pochanart et al., 2003; Geng et al., 2008; Han et al., 2011; Im et al., 2013; Al-Jeelani 2014; Nishant et al., 2014). They show high concentrations during night and early morning and low concentrations during daytime. Peak of precursors in early morning hours is mainly caused by traffic. Due to consumption of precursors in the photochemical reactions their concentration starts decreasing while O_3 concentration rises in the afternoon. Photochemical oxidation to form O_3 and dilution of NO_x due to increased boundary layer and reduced traffic during mid-day results in reduction of NO_x. After that precursor concentration starts increasing gradually accompanying the decrease in O_3 until they reach the second peak around late evening and early night (Jun Tu et al., 2007). The diurnal cycle of CO and NO_x are characterized by double peak (morning and evening hours) due to heavy traffic in rush hours (Ran et al., 2009). Vehicular emissions in the evening hours get trap in the decreased surface boundary layer till the early morning hours (Swamy et al., 2012). The morning peaks of NO, NO_2 and NOx are higher in magnitude than evening peak (Pudasainne et al., 2006). The morning peak of NO_2 is observed 1-2 hours after NO peak while O_3 peak is observed 6 hours after NO peak and 5 hours after NO_2 peak. In morning NO get oxidized to NO_2 through a series of photochemical reactions with O_3 while in noon NO_2 reverts back to NO due to photolysis, resulting in O_3 production (Han et al., 2011).

VOCs also show similar diurnal pattern characterized by double peaks in early morning and late evening corresponding to rush hours (Fanniza et al., 2014). At an urban site of

Mexico, Zheng et al., 2013 reported that all aromatics reach daily maximum before noon and were consumed rapidly in the afternoon. The diurnal variations of the aromatics were strongly correlated with each other, indicating similar emission sources. Aromatic compounds such as toluene and benzene which are mainly emitted from vehicle exhausts due to incomplete combustion and fugitive fuel evaporation (Na et al., 2003), explains the pronounced rush hour peak. Ran et al., 2009 in his study at an urban site (Shanghai, China) found that during morning rush hours NMHCs are relatively higher (22 to 1536 ppb) than average total NMHCs ranging from 30 to 784 ppb in daily sampling.

HCHO which is formed as an intermediate in VOCs degradation is also an important precursor of O_3 (Roberts et al., 2001). HCHO shows peak concentration during 12:00-14:00, which gradually decreases and attains lowest concentration in nighttime. HCHO shows its maximum before that of O_3 as HCHO photolysis is a significant source of hydroperoxyl radical (HO_x) which influence the photochemical production of O_3. HCHO was estimated at a rural site in China indicating that HCHO contributed about 20% of total O_3 formed (Xiaoyan et al., 2010).

Besides the photochemical reactions, boundary layer processes and meteorological parameters also play important roles in the process of diurnal variations in O_3 and its precursors. Therefore, the variations in local meteorological conditions, such as wind direction, wind speed, temperature and relative humidity, affect the temporal variations in O_3 and its precursors (Jun Tu et al., 2007). O_3 shows positive correlation with temperature and solar radiation whereas with relative humidity and its precursors negative correlation is observed (Pudasainee et al., 2006; Mahapatra et al., 2012). Wind speed reflects the turbulence of the boundary layer. During night time, because the boundary layer descends and remains low until early morning and more stable atmospheric conditions exist, the air in the surface layer resists to mixing with that in the upper layer. It is very hard for ambient air pollutants to disperse; thus they are trapped in the shallow surface layer and show high concentrations. This is particularly true for low-level emissions. After sunrise, the heating of the earth surface by solar radiation causes the air to become unstable and to

rise. The boundary layer height and wind speed start increasing and reach the maximum value at noon. With the boundary layer height and wind speed increasing, the dispersion of precursors accelerates and the mixing of the low O_3 concentration air in the surface layer with the higher O_3 concentration air in the upper layer also gets faster (Lal et al., 2000).

Seasonal variation studies of O_3 show maximum concentrations in summer and minimum in winter (Singla et al., 2011; Hassan et al., 2013; Gaur et al., 2014). Higher concentrations are observed in summer due to photochemical oxidation of precursors favored by strong solar radiation and higher temperatures. At Delhi Jain et al., 2005 reported monthly average maximum concentrations in dry summer (62ï 95 ppb) as compared to 50ï 82 ppb in autumn. Inadequate availability of solar flux, high relative humidity and wet surface deposition of air pollutants during monsoon results into lower O_3 concentrations in comparison to summer and winter (Jeelani 2014). In contrast seasonal variation of O_3 at an urban site Ahmedabad showed that O_3 concentrations in autumn and winter months were higher, while those in summer months were lower (Lal et al., 2000). Nishanth et al., 2014 reported highest O_3 concentration in winter (44±3.1 ppbv) while lowest in monsoon (18.5±3.5 ppbv) at a rural coastal site at Kannur, India. The highest O_3 observed in winter is attributed to a lower mixing height that results in trapping of pollutants near the earthôs surface due to temperature inversion (Debaje et al., 2006).

Seasonal trend of NO_x shows maximum in winter and minimum in summer. During winter the lower removal rate of NO_x by reaction, lower boundary layer and low OH concentrations favors high concentrations while higher reaction rate in summer results in low NO_x concentration (Ran et al., 2009). CO also exhibits similar temporal and seasonal pattern (Ahammed et al., 2006). Beig and Singh, 2007 observed the seasonal variation of precursors NO_2, NO and CO at a semi urban site in Pune. Higher concentrations of precursors were found in winter and lower concentrations in summer. Shao et al., 2009 also observed similar trend of precursors at an urban site in Pearl River Delta (PRD), China. NO_x is found to be relatively higher in winter than summer season because of lower removal rates by reaction at lower temperature, lower OH concentration and lower

vertical distribution due to shallow boundary layer. In summer higher temperature favors fast removal of NO_x by high reaction rates (Ran et al., 2009).

Seasonal pattern of VOCs also show peak values in winter and lowest concentration in summer (Fazzini et al., 2014). Guo et al., 2007 observed seasonal variation of VOCs in Hong-Kong, toluene concentration was highest in winter at urban and suburban sites considering that there is more photochemical consumption of toluene in summer due to higher abundance of the hydroxyl radical (OH) however at rural site its concentration is highest in summer, this is likely related to higher evaporation of fossil fuel in summertime. Significant numbers of anthropogenic VOCs were observed to be correlated well with CO emissions in cities throughout the United States, indicating their similar origin and association with vehicular emissions (Baker et al., 2008). The concentrations of the VOCs varied greatly among cities, but the VOC to CO ratios were remarkably similar among the cities. Shao et al., 2009 reported high concentrations of VOCs at PRD, China in summer as higher temperature facilitates evaporative emission of VOCs from fuels and solvents.

Cheng et al., 2014 investigated the seasonal and diurnal variations of carbonyl compounds at roadside, urban and suburban sites in Hong Kong. The average total quantified carbonyl concentrations decreased in the order of roadside (12.16± 3.52 mg m^{-3}), urban (10.45 ±4.82 mg m^{-3}) and suburban (5.14 ± 3.35 mg m^{-3}). Formaldehyde was the most abundant species, accounting for ~52%, ~52% and ~46% of total measured carbonyls at road side, urban and suburban site respectively. Good correlations were found between most carbonyls and CO, showing primary vehicular emission was the major source at the roadside location. In contrast, the summer/winter ratios of most carbonyls were larger than one at the urban site and the carbonyls correlated well with secondary pollutant of O_3, indicating photochemical reactions contributed significantly in the formation of carbonyls, especially in summer. HCHO is attributed by the incomplete combustion of methane used in vehicles that is catalytically converted to formaldehyde in the exhaust pipe. Christensen et al., 2000 investigated that the large photochemical production of formaldehyde and acetaldehyde during summertime from the reaction of ozone and OH-radicals with

hydrocarbons (both natural and anthropogenic) is counterbalanced by the rapid photochemical loss processes due to photolysis and reactions with OH-radicals. The result is that the net production of formaldehyde and acetaldehyde is low during summertime.

The VOCs reactivity is an important factor to determine the ozone formation (Ran et al., 2009; Cai et al., 2010). Because ozone photochemical formation is initiated by reactions of VOCs with hydroxyl radical (OH), the product of VOC concentrations and the OH reaction coefficients is called the reactivity of VOCs. Several reactivity scales are introduced to measure the relative O_3 forming capacity of different non-methane organic compounds (NMOCs). Incremental Reactivity (IR) is a widely used scaling method, defined as the amount of ozone formed per unit of NMOC added or subtracted from the whole mixture in a given air mass (Atkinson, 2000). The Maximum Incremental Reactivity (MIR) method takes into consideration the chemical mechanisms and impacts of NMOC/NO_x ratios on ozone production. Depending upon concentration of NO_x and VOCs, ozone formation is NO_x sensitive and VOC sensitive. It is considered as NO_x sensitive when the NMOC/NO_x ratio is over 8:1 and NMOC sensitive when this ratio is less than 8:1 (Cai et al., 2010; Ran et al., 2009). Na et al., 2003 evaluated the photochemical potential of C_2ï C_9 hydrocarbons at a semi-urban site Seoul (South Korea) by using the maximum incremental reactivity. The contribution made by ethylene to the total specific reactivity was the highest, followed by propylene, 1,2,4-trimethylbenzene, toluene and m/p xylene. It was found that alkenes were the most important contributor to photochemical ozone formation in the vehicle emissions.

High tropospheric O_3 levels has lead to lower crop yields and inferior crop quality leading to economic losses (van Dingenen et al., 2009; Avnery et al., 2011a, b). India being an agricultural dominant country is getting affected by O_3 related crop yield losses. A recent study at Punjab and Haryana during 2011-2013 reported O_3 related crop yield losses for wheat, rice, maize and cotton (Sinha et al., 2015). AOT40 (Accumulated exposure over a threshold of 40 nmol mol^{-1}) and M7 (Mean daytime surface O_3) matrices were used to estimate the cropï yield losses. Relative crop yield losses for wheat, rice, maize and cotton

were 27 to 41%, 21 to 26%, 3 to 5% and 47 to 58% respectively.

In recent years O_3 air quality monitoring is investigated using satellite measurements providing long range transport and global context for changing atmospheric composition (Bowman, 2013). To compare the reported data of O_3 and its precursors various satellite based and model observations studies are being conducted (Beig and Singh, 2007; Zoogman et al., 2011; Marey et al., 2013; Zhang et al., 2014). Srivastava and Sheel, 2013 studied the impact of biomass burning over Indonesia on CO and O_3 enhancement by using MOPITT (Measurements of Pollution in the Troposphere), ozonesonde measurements and 3D chemical transport model MOZART (Model for Ozone and Related chemical Tracers) over 10 year time series. Average CO mixing ratios at 500 hPa, 400 hPa and 300 hPa pressure levels were about 100-250 pppbv higher than average CO mixing ratio (80 ± 12 ppbv). This was due to intense biomass burning observed over Indonesia region. To compare the CO observations MOZART was applied which showed higher values as all the emissions were applied in the model. Zoogman et al., 2011 used geo-stationery satellites for measuring O_3 and CO to monitor the surface O_3 air quality over North America. To study the contributing factors affecting tropospheric CO levels over Alberta, Canada in period 2002-2013 a multi-spectral product NIR and TIR radiance from MOPITT was used. The seasonal cycle of CO showed similar pattern (maximum in winter and minimum in summer). MOPITT values were found to be less than ground data as MOPITT surface values are layer average values and also due to less sensitivity of MOPITT for surface measurements (Marey et al., 2013).

The Indo-Gangetic Plain is densely populated and most polluted region over the globe. The Indo-Gangetic Plain (IGP) stretching from Indus river in north west to delta of Ganga river in west-east direction, Himalayan range in northern border and Deccan plateau in south is affected by anthropogenic and biogenic emission sources. The diverse emission sources industries, bio-fuel burning, themal power plants and crop-residue burning in the IGP results in higher higher pollutants levels as compared to other regions. Agra being in the middle of this region is an important site to study the chemistry of ozone and its

precursors.

In lieu of the review of the studies carried out in India, the present study is proposed to measure surface O_3 and its precursors at a semi-urban site Agra in the IGP region using ground based measurements, meteorological parameters, backward trajectory analysis and satellite based observations. Satellite based monitoring is a complementary approach to monitor emissions and transport of O_3 and its precursors to arrive at an overall picture of O_3 and its precursors in global context with special reference to air quality, long range transport and episodic events.

OBJECTIVES

A comparative study of ground based measurements and satellite observations will be done to monitor emission and transport of O_3 and its precursors.

With this in view the present study has been designed with the following objectives:

- Study of diurnal and seasonal variation of O_3 and its precursors (CO, NO_x, HCHO).

- Determination of some representative VOCs, their seasonal variations and their O_3 formation potential.

- To relate the variations in O_3 levels to meteorological parameters (solar intensity, wind speed, wind direction, temperature) and backward trajectory analysis.

- Inter-comparison of ground based measurements of O_3 and its precursors with spatial distribution and time altitude profile of OMI (Ozone Monitoring Instrument) and MOPITT (Measurements of Pollution in the Troposphere) data.

- To determine the effect of O_3 concentration on crop yield (wheat, rice etc.) through indices like AOT40 (Accumulated exposure over a threshold of 40 nmol mol^{-1}) and M7 (Mean daytime surface O_3).

METHODOLOGY

SITE DESCRIPTION

Sampling will be carried in Science Faculty, Dayalbagh Educational Institute, Dayalbagh, Agra. Agra is located in the north central (27°10' N, 78°05' E) part of India which is about 200 km southeast of Delhi and lies in the middle of Indo-Gangetic Plain. Climatically, Agra is hot and dry during the summer and cool in the winter. The annual rain fall is about 650 mm with 90% being received during monsoon season (Julyï September).Winter is associated with greater calm periods while during the summer and monsoon strong surface winds are observed. Maximum and minimum temperatures in summer are normally 45°C and 25°C, respectively, while in the winter it ranges between 10°C to 3°C. Relative humidity is highly variable from 25ï 99%.

Apart from the local sources Mathura refinery and Firozabad glass industries are both situated at a distance of 40 km from Agra. National Highway lies about 2 km from the sampling site. Although there are no industries in the immediate vicinity of the sampling site, during the monsoon, site becomes downwind with respect to the cityôs pollution sources.

SAMPLING

O_3 and NO_x Measurement: Surface O_3 and NO_x concentration will be recorded using continuously operating O_3 analyzer (Thermo Fischer Model 49i) and NO_x analyzer (Thermo Fischer Model 42i). The ozone concentration measurement is based on ultraviolet absorption photometry; the principle is that ozone (O_3) molecules absorb UV light at a wavelength of 253.7 nm. The absorption of UV-light by O_3 molecule is directly related to the ozone concentration (Beer-Lambert law). Calibration of the system is done with the help of a built-in ozone generator and zero air generator. There is an ozone scrubber which removes ozone from the air supplied by a zero air generator and it acts as a reference. The sample is drawn through the sample bulkhead and is split into two gas streams. One gas stream acts as reference gas, flows to the reference solenoid valve. Other

stream i.e. the sample gas, flows directly to the sample solenoid valve. The solenoid valves alternate every 10 seconds. The NO_x analyzer operates on the principle that nitric oxide (NO) and ozone (O_3) react to produce a characteristic luminescence with intensity linearly proportional to the NO concentration. An infrared light emission occurs when electronically excited NO_2 molecules reaches its ground state. NO_2 is converted to NO by molybdenum NO_2 to NO converter. Molybdenum has ~100% conversion efficiency. The detection limit of O_3 and NO_x analyzer is 0.5 ppb and less than 50 ppt respectively. Calibration will be done by using multipoint calibrator (Teledyne Model T700).

CO Measurement: Surface CO will be recorded using continuously operating CO analyzer (Model T300). The analyzer works on the principle, Beer-Lambert Law by absorbing an IR radiation at 4.67 µm (vibration-rotation band of CO). The T300 uses a high-energy heated element to generate a beam of broad-band IR light with known intensity. This beam is directed through multi-pass cell filled with sample gas. The sample cell uses mirrors at each end to reflect the IR beam back and forth through the sample gas a number of times. The total length that the reflected light travels is directly related to the intended sensitivity of the instrument. Finally, the beam strikes a solid-state photo-detector that converts the light signal into a modulated voltage signal representing the attenuated intensity of the beam. The detection limit of analyzer is 0.04 ppm. The analyzer is calibrated with multipoint calibrator (Teledyne Model T700).

VOC: Sampling will be carried out by active grab sampling method. A battery operated portable sampling pump (SKC 224-XR) will be used to draw air at the rate of 500 ml min^{-1} through SKC adsorption cartridge containing activated charcoal (60ï 80 mesh). The sampling pump will be calibrated by an electronic digital flow calibrator. On an average two samples will be collected every week. Extraction of samples will be done in CS_2. Protection of the exposed charcoal tubes is a very important part of the VOC determination method. The sample tubes will be placed in polythene bags that seal tightly and kept in a box in a freezer until analysis. Analysis will be done by Shimadzu gas chromatograph (GC-17 A) equipped with a flame ionization detector (FID), BP1 capillary column (25m length and 0.3mm internal diameter), and GC Solution software. Analyses will be performed by injecting 1 µL of extract in a splitless port at 180°C with a split of 5

ml min^{-1} and a helium flow rate of 1.2 L min^{-1}. The oven temperature of the GC will be initially held at 40° C for 5min, then raised to 140°C at a rate of 6°C min^{-1} and then raised again to 220° C at a rate of 15° C min^{-1} and held at that temperature for 8min.

HCHO: Formaldehyde will be analyzed by Nash method colorimetrically. Sampling will be done in distilled water in impingers at a flow rate of 1 L min^{-1}. Analysis of the collected samples will be performed with a 1:8 mixture of the Nash reagent (0.02M acetylacetone, 0.05M acetic acid, 2M ammonium acetate buffer) and sample. The yellow coloured product diacetyl dihydrolutidin (DDL) formed by the reaction of Nash reagent with formaldehyde. The interference of higher aldehydes is negligible, since they react with the Nash reagent more slowly and also their absorption spectra are shifted with respect to 412 nm.

AOT40 and M7: This study includes estimation of the loss of wheat and rice crops based on in-situ observations of ozone. AOT40 (accumulated ozone-exposure over a threshold of 40 nmol mol^{-1}) and M7 (mean 7-hour ozone mixing ratio) are the two commonly used metrics for studying the effect of ozone on crops. AOT40 is calculated as the sum of differences between the hourly mean concentration (O_3) and 40 ppb for hours when O_3 > 40 ppb.

$$\mathbf{AOT40 = \Sigma ([O_3]_i - 40)}$$ for $[O_3]$ >40 nmol mol^{-1} during daylight hours only

M7 indice is calculated over 3 consecutive months of a crop growing season, and is defined as the mean daytime 7 h (M7) surface ozone concentrations. This indice differs from AOT40 in that it applies equal weighting to all ozone concentrations to which the crop is exposed.

$$\mathbf{M7 = 1/n \Sigma [O_3]_i}$$ for 09:00-15:59 LT.

In this study, for wheat crop hourly data of ozone from January to April and for rice crop hourly data from July to October will be used as these months are the growing seasons of the respective crops.

The ozone-exposure-dose-response functions for relative yields (RY) for rice and wheat crops based on field studies are given below:

a) Wheat

$RY = e^{-(M7/137)^{2.34}} / e^{-(25/137)^{2.34}}$ (Lesser et al., 1990)

$RY = -0.0000161*AOT40+0.99$ (Mills et al., 2007)

b) **Rice**

$RY = e^{-(M7/202)^{2.47}} / e^{-(25/202)^{2.47}}$ (Adams et al., 1989)

$RY = -0.0000039*AOT40+0.94$ (Mills et al., 2007)

Crop production loss (CPL) is calculated based upon the relative yield loss, and the production output data:

$$CPL= RYL/(1- RYL)*CP$$

The annual crop yields (CP) for wheat and rice will be taken from the Department of Agriculture and Co-operation, India (source: http://aps.dac.gov.in/APY/Public_Report1.aspx) for the respective year for Agra region.

Satellite based Observations: A comparative study of surface measurement of ozone and CO will be done with latest retrievals of satellite measurements. For satellite data MOPITT (Measurements of Pollution in the Troposphere) and TOMS (Total Ozone Mapping Spectrometer) instruments on board, Terra and Aura satellites of NASA will be used. Satellite observations for O_3 will be done by NASA-EOS-Aura satellite. The OMI (Oone Monitoring Instrument) onboard is a nadir viewing wide swath UV/VIS hyperspectral spectrometer (resolution 13km x 24 km) measuring the solar light reflected and backscattered from the Earthôs atmosphere and surface in the wavelength range from 270 nm to 500 nm with a spectral resolution of 0.45 nm in the ultraviolet and 0.63 nm in the visible.

For CO measurements MOPITT will be used which is a thermal and near-IR nadir-viewing gas correlation radiometer. MOPITT uses a cross-track scan which allows for almost complete coverage of the Earthôs surface in about 3 days, with individual pixels of 22km x 22km horizontal resolution. In present study only daytime MOPITT retrieval by NIR channels will be used because in night only TIR channels are used which are not sensitive to near surface measurements.

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